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SENSITOMETRIC STUDY OF
IO-BROMIZED DAGUERREOTYPE PLATES

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ABSTRACT

This research deals with a study of speed and contrast of daguerreotype plates that receive varying levels of sensitizing to the fumes of iodine, then bromine, and finally, a second iodizing. This sensitizing operation along with mercury development and gold gilding are characteristic of the process in its most improved state.

Statistical analysis reveals how iodizing and bromizing affect speed and contrast. A field study was conducted to relate the sensitometric data to images produced in the camera.

The experiment suggests an exposure index of .05 for the optimum in speed. This would correspond to an exposure of roughly 1 second at f/4.5 on a bright, sunny day.

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INTRODUCTION

The daguerreotype was the first successful form of photography that became widely used. Its development took over 20 years of research spent between the Frenchman Nicephore Niepce and Louis Daguerre (1). The process was announced to the public in January of 1839 and rapidly grew in popularity.

Briefly, Daguerre's process is as follows; a highly polished plate made of copper and having a thin coating of silver is subjected to the fumes of iodine, forming a very thin layer of silver iodide. After exposing the plate, it is developed over heated mercury. The mercury vapor selectively condenses onto the latent image in proportion to exposure. The plate is then fixed in a solution of sodium thiosulfate.

Photographic Characteristics

The greatest dissimilarity between modern films and the daguerreotype comes from the absence of protective gelatin on the daguerreotype plate. The plate is only sensitive to ultraviolet, violet, and some blue radiation.

The image, being fine droplets of mercury, amalgamated at the silver surface, is easily wiped off the plate and must be protected under glass.

Latent image fading occurs rapidly at room temperature

and its effects can be seen after only a 15 minute interval between exposure and development.

The daguerreotype plate exhibits density by varying the degree of specular reflection. The viewing geometry is illustrated in figure 1.

Historical Improvements

Several improvements were made to Daguerre's original process within 1840. It was found that a combination of iodizing, bromizing, and then a brief iodizing increases speed by a factor of 100. Original daguerreotypes had an exposure index of about .0008 (2). Gold gilding (Fizeau) was a technique that stabilized and accentuated the image and gave warmer tones (3). The daguerreotype process was essentially replaced by wet collodion emulsions during the 1850's (4), however references hint that the process has always been practiced by someone up to the present time.

Dr. Draper, a 19th century chemist, theorized that the color changes a daguerreotype plate goes through while being fumed accounts for its degree of sensitivity (5). While the plate went from faint to deep yellow, it absorbed more blue radiation and increased in sensitivity.

Irving Pobboravsky (1971) expanded on Draper's hypothesis by examining the cause of color found on the plate and the plate sensitivity as a function of silver iodide

thickness. He also examined the Becquerel technique of processing without mercury. His research indicates that the color seen on iodized daguerreotype plates are not due to a single cause but represent a very complex optical problem involving interference, scattering and possibly absorption.

Due to the lack of sensitometric methods in the daguerrean era, there is still much to be learned about the process. In the present day there is growing interest in daguerreotypy and there are now more people attempting the process than there has been in the last one-hundred years. For these reasons it is of great interest to study the process in its most improved form and in a systematic manner.

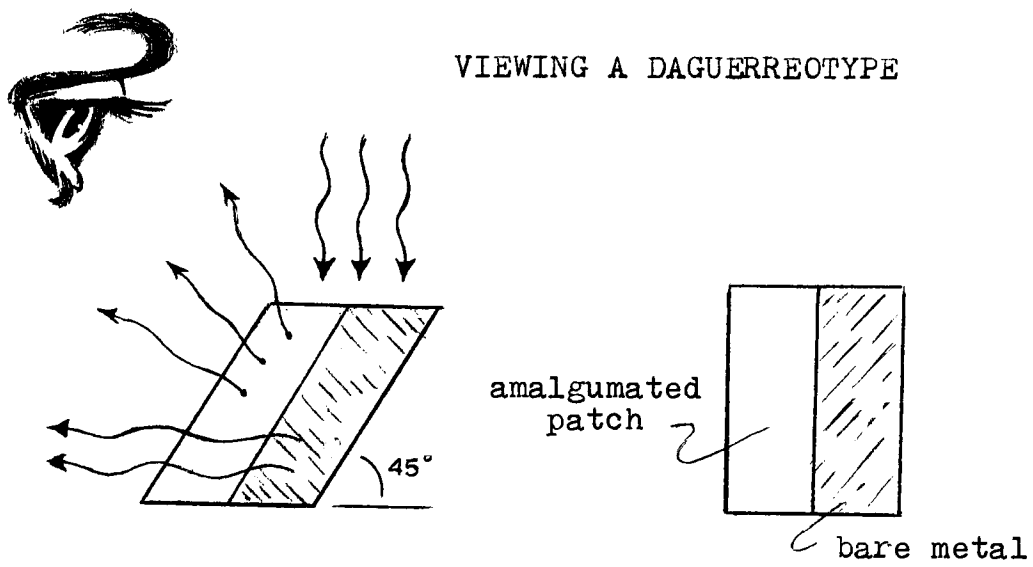


Figure 1

Figure 2

3^3 FACTORIAL DESIGN

	I ₁			I ₁			I ₁		
	Br	Br	Br	Br	Br	Br	Br	Br	Br
I ₂									
I ₂									
I ₂									

EXPERIMENTAL

To study the sensitometric characteristics of the daguerreotype plate, namely speed, contrast, minimum and maximum density, as a function of sensitizing treatment, a 3 factor experiment was used. The experiment design consists of 3 factors; that of 1st iodizing, bromizing, and 2nd iodizing each represented at 3 levels of sensitizing time. The design outlined in figure 2 allows for complete interaction among factors using the fewest number of plates.

The 27 plates were processed according to a standardized procedure. Some of the special equipment used in the experiment are pictured in figures 3 & 4.

Polishing

The first step taken was to polish the plates. The purpose of buffing is two fold. First, it removes all foreign matter including oxidation from the silver surface. Secondly, it attempts to remove all scratches from the surface which reduce the amount of specular reflection (7). A well prepared plate will have a maximum density greater than 2.00.

The plates were of good quality engravers brass electroplated with a 7 micron silver layer. The plates

were bathed in methynol prior to polishing to remove all grease and then buffed with chromium oxide followed by red rouge (ferric oxide). A final buff on chamois was given just prior to sensitizing which removed any oxidation. To remove an image and re-use a plate, 1200 mesh emery preceeded the above mentioned steps.

Sensitizing

The sensitizing and mercurizing operations were conducted under a laboratory fume hood due to the toxic nature of bromine and mercury.

The plates were sensitized to iodine in a box using a slide arrangement with very little escape of iodine from the box. It was found that the iodine fume concentration remained stable from day to day at a given room temperature. Three levels for each sensitizing factor had to be determined. Pobboravsky found the speed of an iodized plate to increase as it went from pale yellow to yellow-magenta and decrease thereafter. From this information the middle level was chosen to be 40 seconds, as this produced a yellow magenta. The lower level was chosen at 25 seconds and the high level at 60 seconds.

Bromizing was accomplished by injecting bromine water into a box, (Figure 5) and allowing 1 minute for the fumes to accumulate before sensitizing. The factors involved with achieving different levels of bromizing are : dilution,

sensitizing time, temperature and bromine concentration. By experimentation, it was found that 5 ml of bromine water in 5 ml water gave good results using only time of sensitizing as the variable. The results of these alterations gave 3 levels which produce significant but drastic changes in speed. Figure 6 illustrates this change.

The 2nd iodizing level is found in the literature to be some fraction of the 1st iodizing ranging from $1/10$ to 1 (8). For the experiment the three levels of I_2 were chosen to be $1/5(I_1)$, $1/2(I_1)$, and $1(I_1)$.

Exposure

An enlarger having a 100 watt tungsten bulb was used as a light source. The enlarger was in line with a voltage regulator and produced 200 lux incident on a contact printing frame as measured with a UDT meter. A 20 second exposure time was used throughout the experiment. A step density tablet with .3 increments modulated exposure. The tablet had to be kept free of grease because fingerprints easily transferred to the plate and prevented development.

Development

The working mechanism of the mercury box is illustrated in the appendix, but briefly, the box was designed to quickly reach a development temperature of around 50° - 60° C and remain as constant as possible.

Approximately 3 ml of mercury was placed in a copper cup and a fine mesh cloth was stretched over the cup to prevent minute mercury drops from splashing onto the plate.

Initially 50°C was chosen to develop plates, however weak images resulted even with development times of 8-12 minutes. By raising the temperature to 60°C, development times of 2-6 minutes gave adequate results. A closer examination of development yielded 4 minutes as an optimum when used at 60°C. Figure 7 illustrates the decrease in D_{\max} and D_{\min} that occurs with increasing development.

Finishing

After development the plates were fixed in a solution of sodium thiosulfate (15 grams/500 ml) and then rinsed in distilled water.

A gold chloride ($\text{AuCl}_3\text{HCl} \cdot 3\text{H}_2\text{O}$) and sodium thiosulfate solution was used to gild the plates. The gilding operation consists of mixing equal amounts of the 2 solutions, applying it to the plate which lies in a pan, applying the heat of an alcohol lamp for approximately 2 minutes until the image assumes a bolder appearance and then rinsing with distilled water. The plate must not be allowed to come in contact with air until after gilding and the following rinse because oxidation causes mottling (9).

Once all the plates had been processed they were measured using a Macbeth RD-100 reflection densitometer.

This has a working geometry very similar in the way a daguerreotype is viewed. The results for each plate were then plotted. The slope, relative speed, minimum and maximum densities, were recorded for each treatment.

Once preliminary experiments were completed, the factorial design experiment was done in 3 days to reduce error due to long range variability. The experiment was limited to a half replicated one because of time and expense limitations. However, the first 4 treatments were replicated to give an indication of variability.

1 emery on velvet buff
 2 chromium oxide on velvet buff
 3 red rouge on chamois buff
 4 chamois buff
 5 box for holding 27 plates

6 alcohol lamp
 7 gilding pan
 8 plate holder
 9 plastic syringe

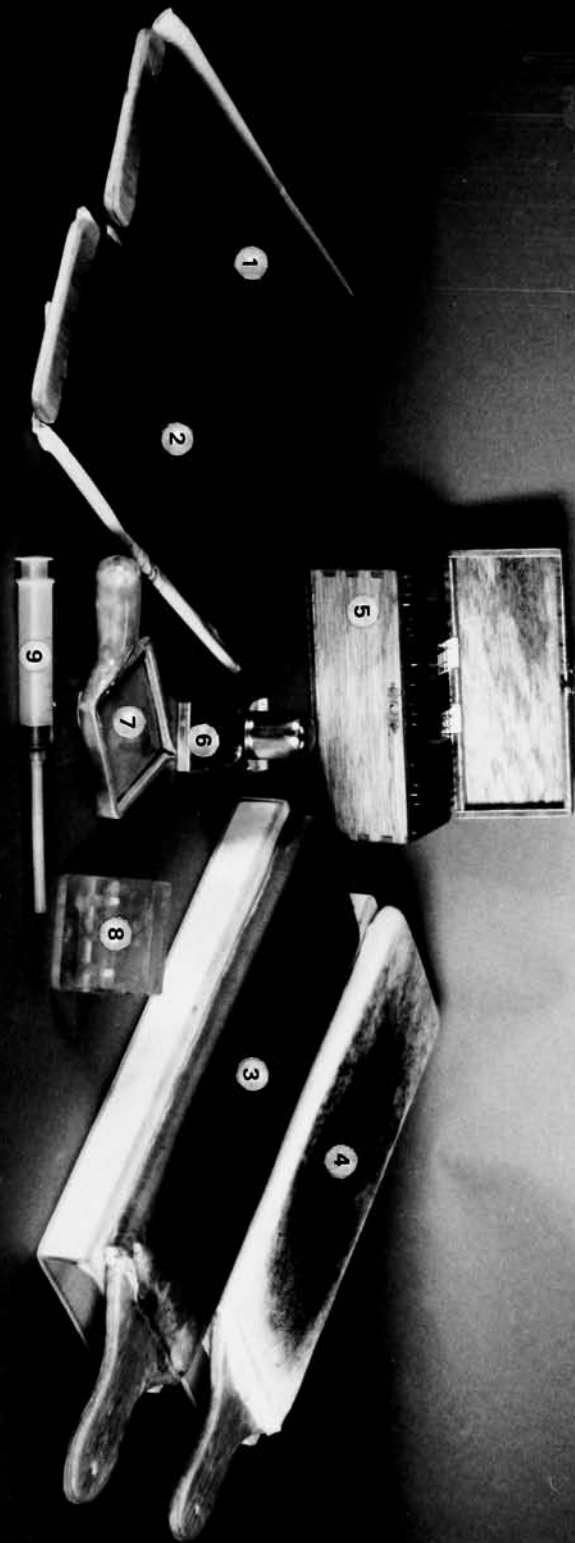
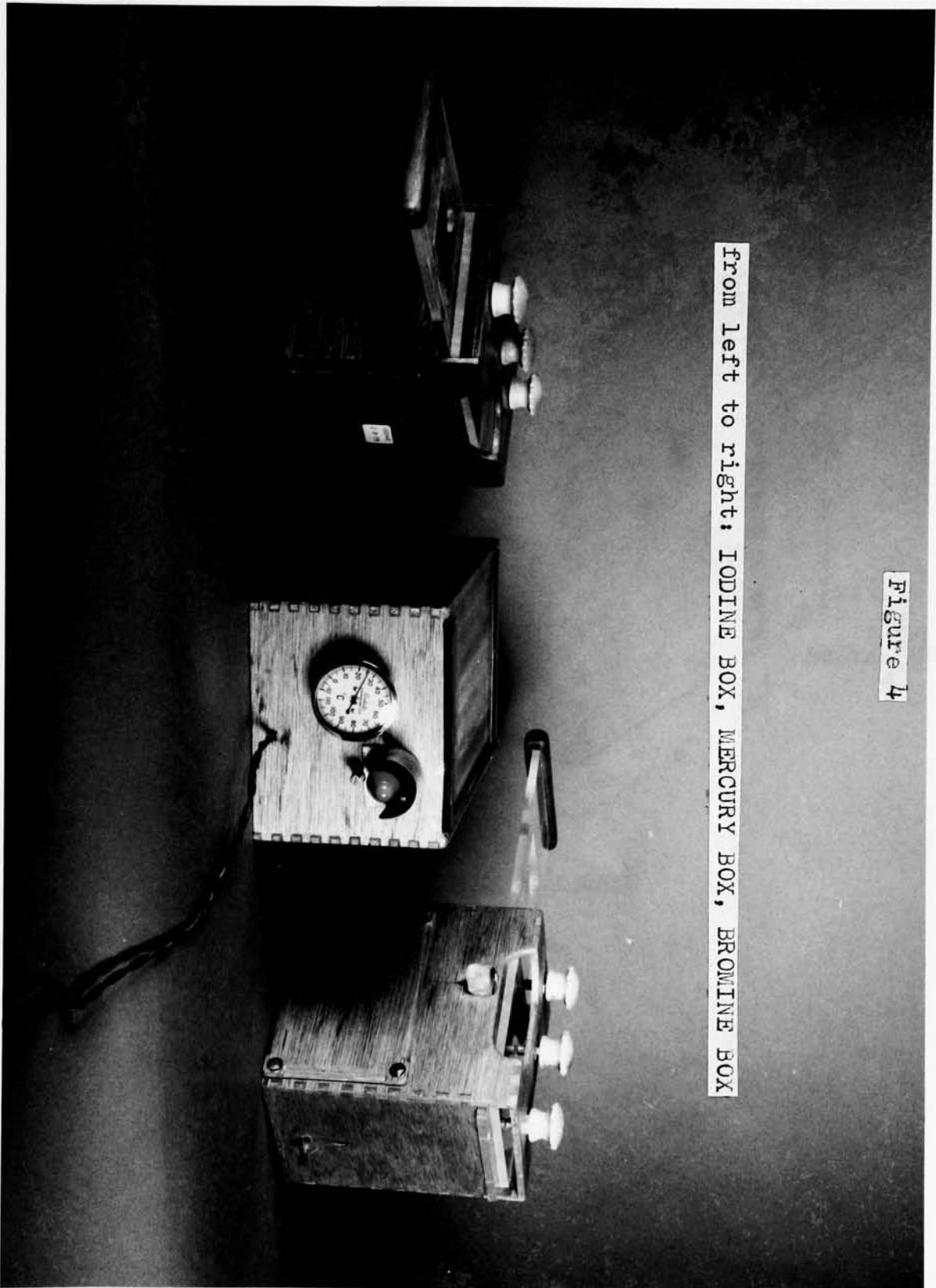


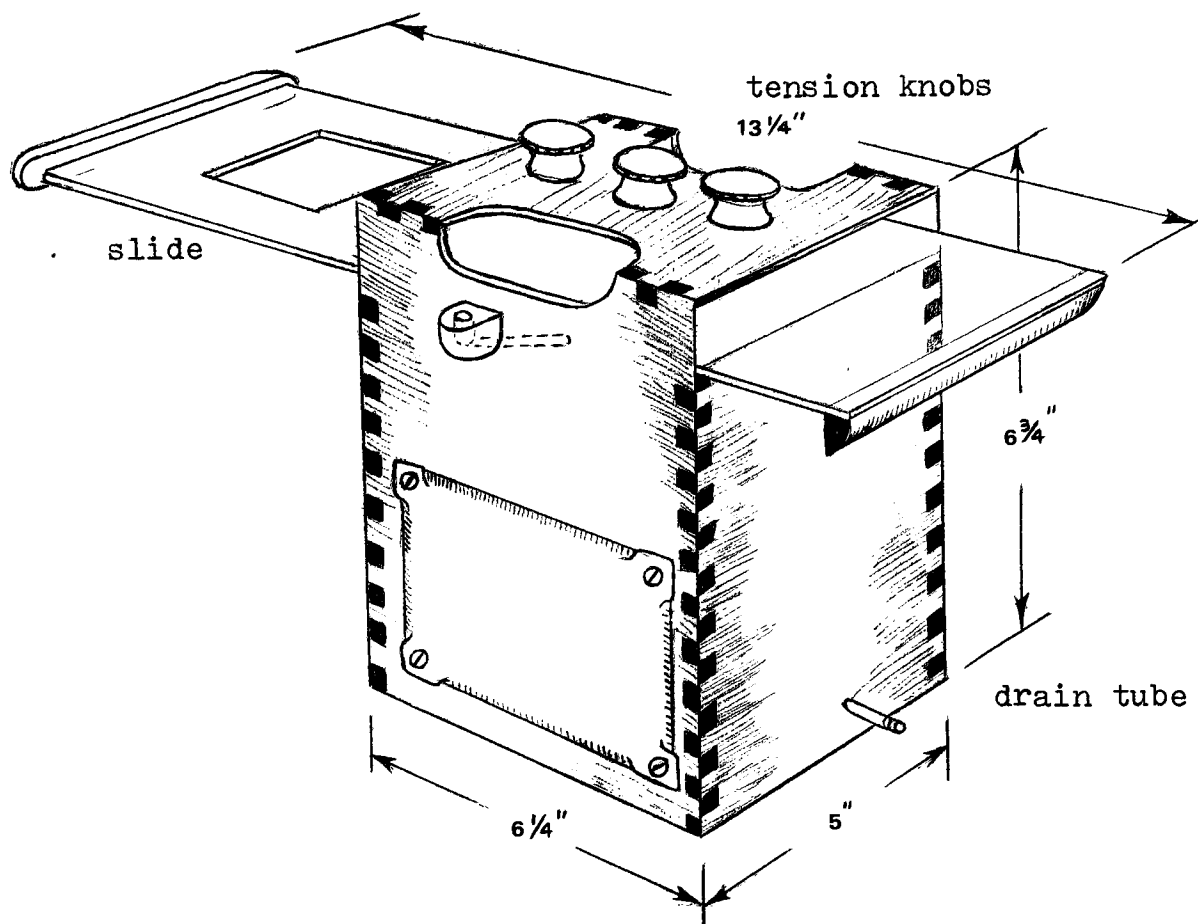
Figure 3

Figure 4

from left to right: IODINE BOX, MERCURY BOX, BROMINE BOX



BROMINE BOX



INNER ASSEMBLY

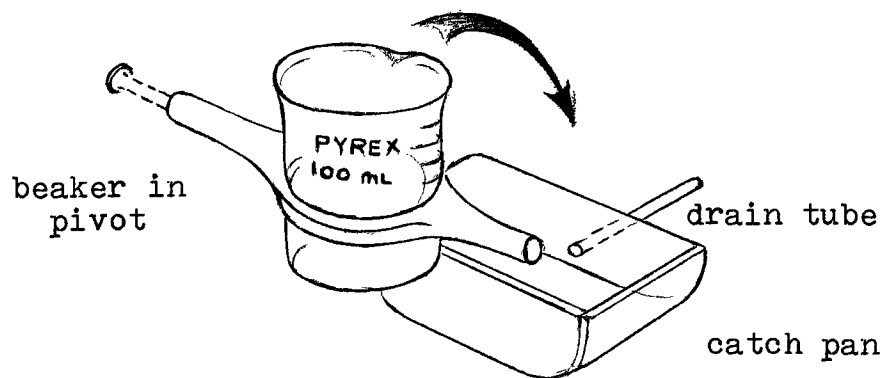
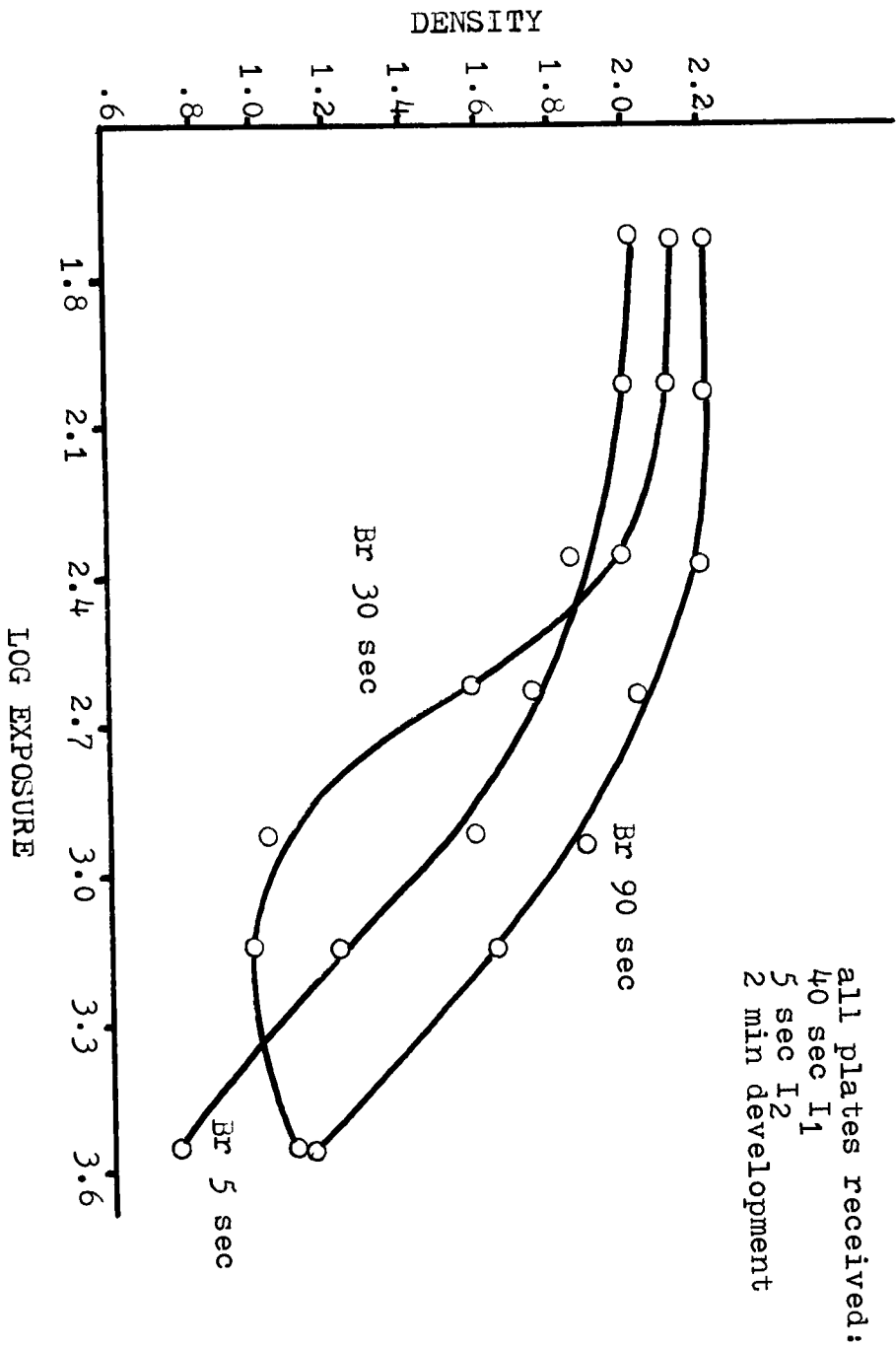


Figure 5

Figure 6

VARYING BROMINE LEVEL



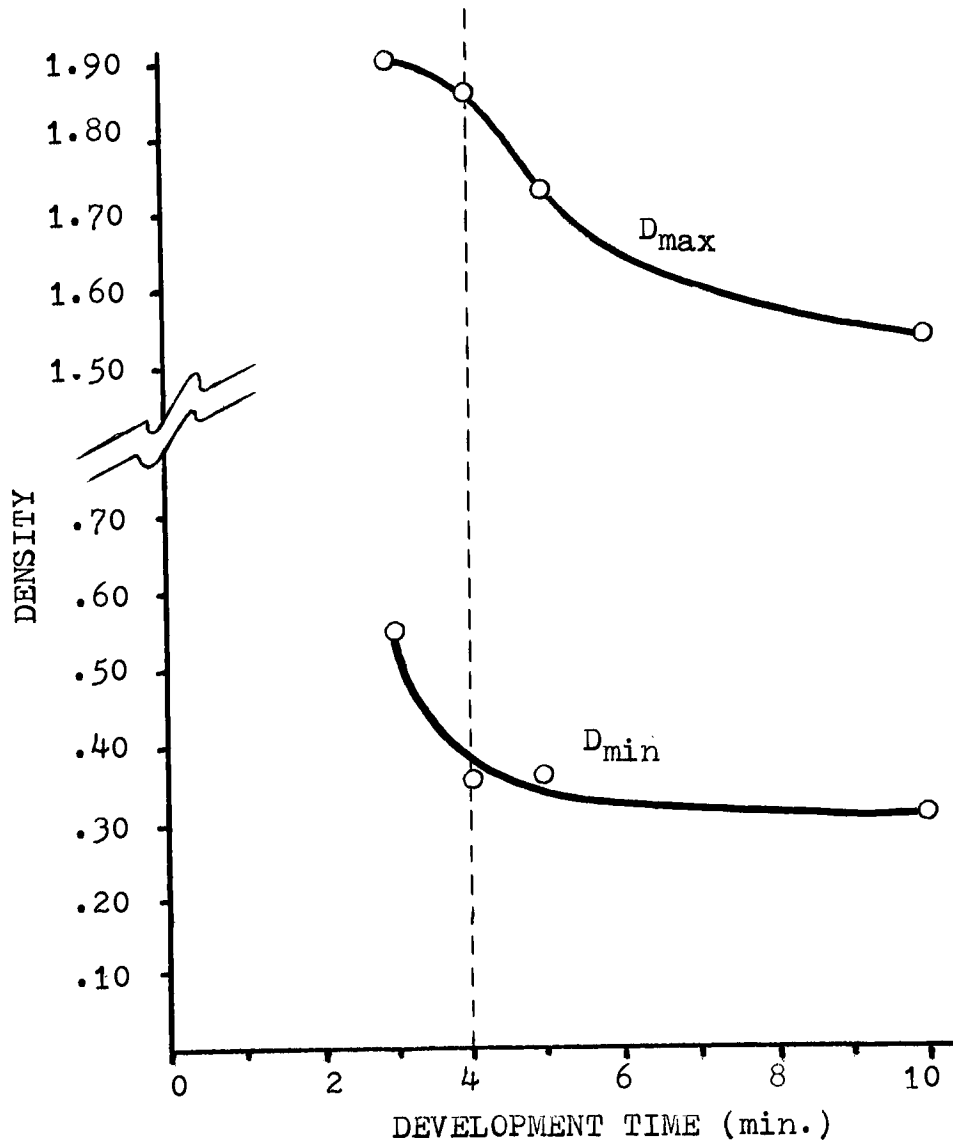
D_{\max} & D_{\min} vs. DEVELOPMENT

Figure 7

RESULTS

The response variables were analyzed using the Yates method (10), a systematic method for calculating effects in a factorial experiment. A computer program in a Hewlett Packard desk computer was used for the analysis. Data is given to the computer in standard order (Figure 8) and the computer prints out the 3 columns, the last one being the desired set of effects totals. The computer then prints out the F-ratio for each factor. The F-ratio is usually a comparison between the sums of squares of each factor and the SS term for error. In this case, the highest order interaction is attributed to error and used in the F ratio since there was no replication and hence no SS term for error. The F distribution is then used to determine the degree of significance of the factor's effect.

Tables 1&2 list the data obtained from the computer analysis, and pertinent critical values of the F distribution. The notation for significance is *, where the alpha is .1, ** for alpha = .05, and *** for alpha = .01. The 1st iodizing, bromizing, and second iodizing are listed by the program as A, B, and C, respectively.

STANDARD ORDER

3-FACTOR, 3-LEVEL FACTORIAL DESIGN YATES METHOD		
MAX DENSITY		
Treatment combinations		Response variable
000	1.62	
100	1.78	
200	2.10	
010	1.90	
110	1.94	
210	2.00	
020	1.78	
120	2.00	
220	1.73	
001	2.00	
101	1.76	
201	2.00	
011	1.78	
111	1.92	
211	2.00	
021	1.90	
121	1.75	
221	2.05	
002	1.93	
102	2.10	
202	1.85	
012	2.15	
112	2.10	
212	2.00	
022	1.80	
122	2.00	
222	1.92	

Figure 8

COMPUTER DATA & CRITICAL VALUES

SS ER	0.18	8 DF	SS ER	0.37	8 DF
MS ERR	0.02		MS ERR	0.05	
D_{max}					
SS R	0.05	2 DF	SS R	0.08	2 DF
MS R	0.02		MS R	0.04	
F-RATIO	1.01		F-RATIO	0.88	
	2,8 DF			2,8 DF	
SS B	0.03	2 DF	SS B	2.06	2 DF
MS B	0.02		MS B	1.03	2 DF
F-RATIO	0.68		F-RATIO	21.97	
	2,8 DF			2,8 DF	
SS C	0.06	2 DF	SS C	0.01	2 DF
MS C	0.03		MS C	0.01	2 DF
F-RATIO	1.29		F-RATIO	0.13	
	2,8 DF			2,8 DF	
SS BE	0.03	4 DF	SS BE	0.09	4 DF
MS BE	0.01		MS BE	0.02	
F-RATIO	0.38		F-RATIO	0.49	
	4,8 DF			4,8 DF	
SS AC	0.15	4 DF	SS AC	0.17	4 DF
MS AC	0.04		MS AC	0.04	
F-RATIO	1.62		F-RATIO	0.90	
	4,8 DF			4,8 DF	
SS BC	0.03	4 DF	SS BC	0.03	4 DF
MS BC	0.01		MS BC	0.01	
F-RATIO	0.36		F-RATIO	0.14	
	4,8 DF			4,8 DF	

Table 1

$$F_{2,8,.1} = 3.11$$

$$F_{4,8,.1} = 2.80$$

$$F_{2,8,.05} = 4.46$$

$$F_{4,8,.05} = 3.84$$

$$F_{2,8,.01} = 8.65$$

$$F_{4,8,.01} = 7.00$$

SPEED

SS ER 217823.85
8 DF
MS ERR 27227.98

SS A 265006.52 2
DF
MS A 132503.26
F-RATIO 4.87**
2,8 DF

SS B 1507615.63
2 DF
MS B 753807.81 (2)
DF
F-RATIO 27.69**
2,8 DF

SS C 38807.41 2
DF
MS C 19403.70 2
DF
F-RATIO 0.71 no sig.
2,8 DF

SS AB 636237.04
4 DF
MS AB 159059.26
F-RATIO 5.84**
4,8 DF

SS AC 78357 26 4
DF
MS AC 19589.31
F-RATIO 0.72 NS
4,8 DF

SS BC 267401.48
4 DF
MS BC 66850.37
F-RATIO 2.46
4,8 DF

SLOPE

SS ER 0.64 8 DF
MS ERR 0.08

SS A 0.58 2 DF
MS A 0.29
F-RATIO 3.60*
2,8 DF

SS B 0.51 2 DF
MS B 0.25 2 DF
F-RATIO 3.16*
2,8 DF

SS C 0.02 2 DF
MS C 0.01 2 DF
F-RATIO 0.15
2,8 DF

SS AB 0 41 4 DF
MS AB 0.10
F-RATIO 1.28
4,8 DF

SS AC 0.13 4 DF
MS AC 0.03
F-RATIO 0.39
4,8 DF

SS BC 0 44 4 DF
MS BC 0.11
F-RATIO 1.37
4,8 DF

COMPUTER ANALYSIS

DISCUSSION

Contrast

The slope of the curve was measured for each treatment. For several plates a straight line portion did not exist, in which case the slope was estimated. In 7 treatments, all at the low bromine level, only the shoulder of the curve was obtained and the slope was determined by 2 data points. Little confidence can be given to this determination concerning slope.

The analysis by the Yates method found both the 1st iodizing and bromizing significant at the .1 level. Using table 3 as a visual check, it can be seen that as I_1 increases, contrast decreases. It was also noted that the tonal quality moved from neutral to warm, brown tones as I_1 increased. The effect of bromizing on contrast is not as apparent, although the middle level is of higher contrast in comparison to the low and high levels.

Speed

Because of the dissimilarities between daguerreotype plates and modern films, different criterion was established in the assignment of a speed value. A speed point was established on the log exposure scale for an exposure which produces a density that is .1 below that of the threshold density. A relative speed of 1000 was assigned to the fastest plate and slower plates took values based on a

geometric progression that halved the value for each log exposure difference of .3. These values can be found in table 4.

The Yates analysis shows I_1 to be significant at an alpha risk of .05. By averaging the speeds in each I_1^- , I_1^0 , I_1^+ block of 9 treatments, it is shown that speed generally increases with an increase in I_1 .

Bromizing has an F ratio of 27.70 which indicates high significance. Also the interaction between the 1st iodizing and bromizing has a significant effect on speed. The effects can better be seen in a three dimensional surface shown in figure 9. This graph illustrates that the areas of greatest speed were centrally located in the experiment.

Minimum Density

The only significant factor for this response is bromine. The average minimum density for the low level of bromine was 1.00. Again, incomplete curves hindered the determination of this value. The average D_{\min} for the medium level was .48 and for the high level it was .51. This trend follows that of speed and suggests correlation, however a low correlation coefficient of .05 was calculated. Table 5 illustrates the significance of bromine.

Maximum Density

The Yates analysis shows maximum density to be

independent of sensitizing factors. The response data is listed in table 6.

Field Test

To relate the data to its useful application, several exposures were made in a Kowa $2\frac{1}{4}$ format camera. Table 7 contains the exposing data and the calculated exposure index for each case. The 40/30/5 (second) treatment was one step slower than the 60/30/12 treatment which agrees with the sensitometric data. It was disturbing however to find these speeds 2 stops slower than what was determined in a field test made 4 weeks earlier in which portraits were made using an exposure index of .025. Two reasons are suggested for this effect. First; bromine water is unstable and could have partially decomposed. Second; later plates were re-used and tests on speed were not conducted concerning the re-use of plates.

Table 3

Contrast




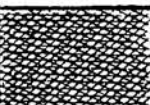


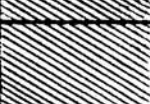







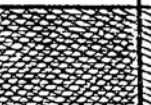





	I_1^-			I_1^0			I_1^+		
	Br^-	Br^0	Br^+	Br^-	Br^0	Br^+	Br^-	Br^0	Br^+
I_2^-									
I_2^0									
I_2^+									



Table 4

Speed

I_1^-				I_1^0				I_1^+			
Br^-				Br^0				Br^+			
I_2^-				I_2^0				I_2^+			
16				40				25			
178				500				200			
354				178				250			
6				45				200			
500				400				800			
1000				316				200			
13				8				16			
1000				1000				1000			
400				200				126			

Figure 9

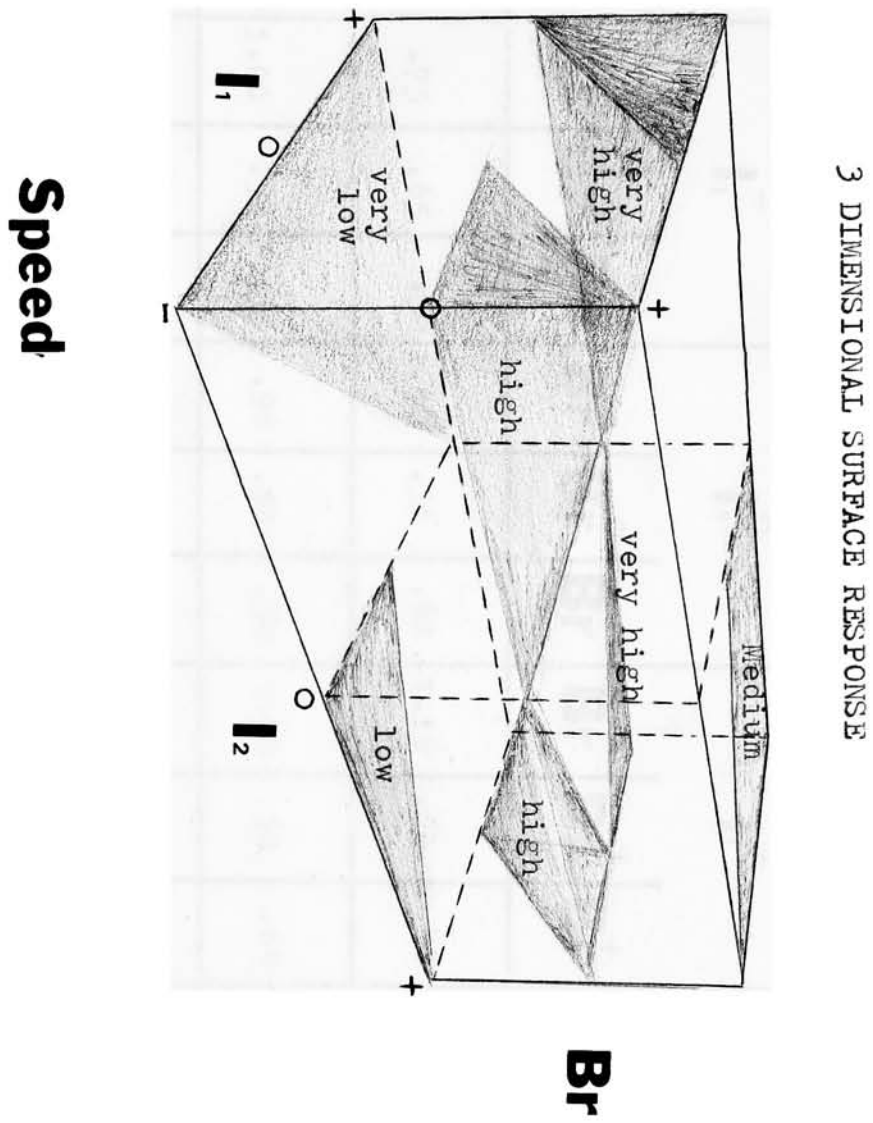


Table 5

D_{min}

I_1^-			I_1^0			I_1^+			
Br^-	Br^0	Br^+	Br^-	Br^0	Br^+	Br^-	Br^0	Br^+	
I_2^-	.75	.65	.50	1.40	.36	.62	1.10	.54	.42
I_2^0	1.00	.32	.58	.90	.50	.50	1.40	.50	.64
I_2^+	1.20	.45	.50	.65	.50	.36	1.30	.48	.48

Table 6

D_{max}

		I_1^-			I_1°			I_1^+		
	Br^-	Br°	Br^+	Br^-	Br°	Br^+	Br^-	Br°	Br^+	
I_2^-	1.62	1.90	1.78	1.78	1.94	2.08	2.10	2.00	1.73	
I_2°	2.00	1.78	1.90	1.76	1.92	1.75	2.08	2.00	2.05	
I_2^+	1.93	2.15	1.80	2.10	2.10	2.08	1.85	2.00	1.92	

Table 7

FIELD STUDY

Gannett Building photograph #1

f/2.8
 15 second exposure
 zone 4*
 e.v. reading = 12.5
 40/30/5 (00-) treatment
 relative speed (500)
 exposure index .0038

Gannett Building photograph #2

f/4.0
 15 second exposure
 zone 4
 e.v. reading = 12.5
 60/30/12 (+0-) treatment
 relative speed (1000)
 exposure index .0076

Portrait

f/2.8
 40 second exposure
 zone 6
 e.v. reading = 13
 60/30/30 (+00)
 relative speed (1000)
 exposure index .0076

*based on Ansel Adams zone system
 which relates meter readings to
 relative scene tones.

CONCLUSIONS

The statistical analysis reveals the effects of iodizing and bromizing on speed and contrast.

1. In general, contrast decreases with an increase in initial iodizing.
2. Increasing the initial iodizing also produces warmer tones and increases speed.
3. Bromizing is a major contributor to the speed of the plate.
4. The exposure index of .025 was calculated for the treatment that had a relative speed of 500. This speed was later found to decrease by 2 stops, the cause of which is not known.

This experiment did not attempt to include a variety of different plates, sensitizing apparatus or laboratory conditions, for an experiment of this type would be immense. However, a person attempting the process could use this data as a guide in evaluating the process.

ACKNOWLEDGEMENTS

I would like to express appreciation for materials and equipment loaned to me by Mr. Walter Horne and Mr. Robert Snyder.

I also would like to thank Mr. Albert Rickmers for his helpful suggestions on the statistical analysis and Miss Susan Mueller for her help on the field study.

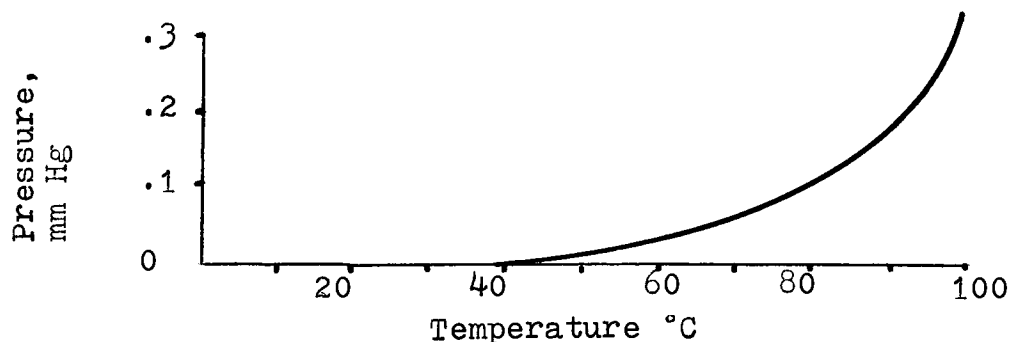
I am greatly indebted to my thesis advisor, Mr. Irving Pobboravsky, whose interest and expertise in daguerreotypy have inspired my efforts.

APPENDIX 1

Mercury

Mercury fumes present a real danger to the daguerreotypist in that the fumes are odorless, colorless, and toxic. The vapor of mercury is mostly filtered by the lungs and accumulates there. The biological half life of mercury in the average human is 20 days. This is the logarithmic decay rate at which the body disposes of mercury. Metallic mercury should not be confused with methyl mercury which is extremely toxic and has a half life of 75 days. The threshold limit value for mercury to which workers may be repeatedly exposed, day after day for a 40 hour workweek, without adverse effect is $.05 \text{ mg/m}^3$ (11). The vapor pressure of mercury rises rapidly after 70°C as can be seen in figure 10. The use of a slide arrangement minimizes fume leakage and when operated under a fume hood insures safe operation.

Figure 10: Vapor Pressure vs. Temperature of Mercury

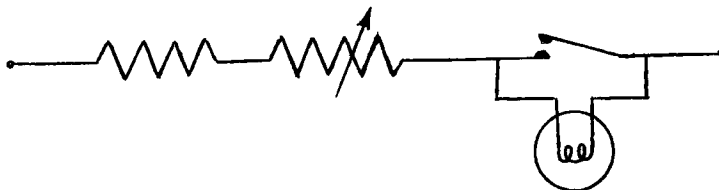


APPENDIX 2

Mercury Box

The mercury box took 12 hours to assemble and consists of the following elements:

1. Copper innerlining (4 sides and bottom) of .032" stock
2. Laboratory heating tape $\frac{1}{2}$ " x 6 ft wrapped around the copper lining.
3. $\frac{1}{4}$ " fiber glass insulation wrapped around the tape
4. Outer shell made from $\frac{1}{4}$ " mahogany ply
5. Plate holder (5"x 7") built into the outer shell
6. Thermometer which measures the air temperature of the interior
7. Thermoswitch, potentiometer, and indicator light (see circuit diagram below)



By using the formula for specific heat capacity:

$c = dQ/(m \cdot dt)$, where dQ is the quantity of heat in watts (joules/sec), m = mass of the copper in grams, and dt is

the change in temperature, the rate of heating can be calculated.

$$c \text{ (copper)} = .093 \text{ (g cal}^{-1} \text{ (}^{\circ}\text{C)}^{-1} \text{)}$$

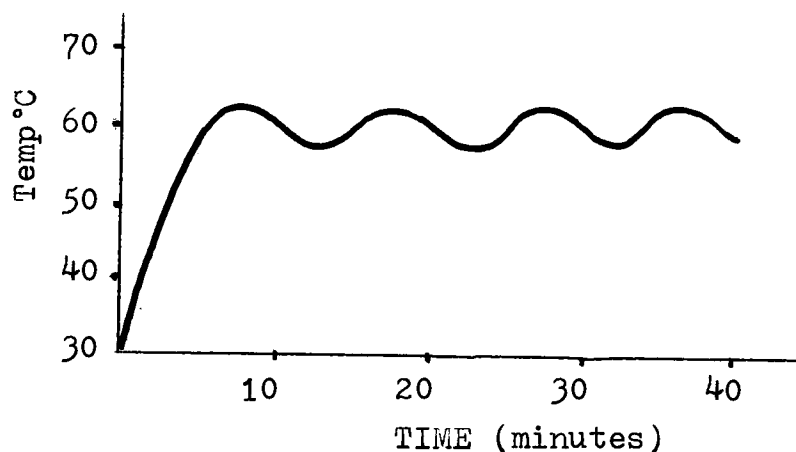
$$m \text{ (copper lining)} = 681 \text{ grams}$$

$$.093 = dQ/681, \quad dQ = 63.3 \text{ cal} = 265 \text{ watts}$$

\therefore 265 watts for 1 sec. raises the temperature 1°C .

This calculation confirmed the rapid heating and large fluxuations that resulted from a high wattage.

The potentiometer was used to reduce the wattage and obtain smaller fluxuations.



A future design of a mercury box might include a heating source that supplies smaller wattage and a more efficient arrangement of the electronic sensing componants that would reduce thermal lag time. Perhaps more insulation would contribute to stability.

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